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Preparation and Characterization of ZnO Nanoparticles: Application to Sensor Devices

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Abstract: ZnO nanoparticles were prepared by precipitation method from zinc chloride. The powder was characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, selected-area electron diffraction, UV-vis optical absorption and photoluminescence spectroscopy analyses. XRD patters showed that ZnO nanoparticles have hexagonal unit cell structure. SEM &TEM pictures reveal the morphology and particle size of prepared ZnO nanoparticles. The UV-vis absorption spectrum shows an absorption band at 355 nm due to ZnO nanoparticles. The photoluminescence spectrum exhibits two emission peaks one at 392 nm corresponds to band gap excitonic emission and another located at 520 nm due to the presence of singly ionized oxygen vacancies. The synthesis method has potential for application in manufacturing units due to ease processing and more economical reagents. *Copyright © 2014 IFSA Publishing, S. L.*

Keywords: ZnO, Nanoparticles, XRD, SEM, FTIR.

1. Introduction

Oxide semiconductor nanostructures have been widely investigated in recent years because of their excellent electrical and optical properties which are highly useful in fabricating nano scaled optoelectronic and electronic devices with multi functionality [1-3]. Among various semiconducting materials, zinc oxide (ZnO) is a distinctive electronic and photonic wurtzite n-type semiconductor with a wide direct band gap of 3.37 eV and a high exciton binding energy (60 meV) at room temperature [4, 5]. The high exciton binding energy of ZnO would allow for excitonic transitions even at room temperature, which could mean high radiative recombination efficiency for spontaneous emission as well as a lower threshold voltage for laser emission. The lack of a centre of symmetry in wurtzite, combined with a large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and hence the use of ZnO in mechanical actuators and piezoelectric sensors [6, 7]. ZnO is potential candidate for optoelectronic applications in the short wavelength range (green, blue, UV), information storage and sensors as it exhibits similar properties to GaN [8-10]. ZnO nano particles are promising candidates for various applications, such as nanogenerators, [11] gas sensors, [12] biosensors, [13] solar cells, [14] varistors, [15] photodetectors, [16] and photocatalysts, [17]. From the literature survey, it was found that various approaches for the preparation of ZnO nano powders have been developed viz., sol-gel, microemulsion, thermal decomposition of organic

precursor, spray pyrolysis, electrodeposition, ultrasonic, microwave-assisted techniques, chemical vapor deposition, hydrothermal and precipitation methods [18-27]. Most of these techniques were not extensively used on a large scale but chemical synthesis has been widely used due to its simplicity and less expensive. In the present study, we report the synthesis of ZnO nano particles using chemical method and the characterization of ZnO nano particles using X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), UV-vis absorbance and photoluminescence spectra is discussed.

2. Experimental Methods

Zinc Chloride, sodium hydroxide and ethanol were purchased and used without further purification. Zinc oxide nanoparticles were synthesized by co-precipitation method using Zinc Chloride and sodium hydroxide precursors. In this experiment, a 0.5 M aqueous ethanol solution of Zinc Chloride was kept under constant stirring using magnetic stirrer to completely dissolve the Zinc Chloride for one hour and 0.9 M aqueous ethanol solution of sodium hydroxide (NaOH) was also prepared in the same way with stirring of one hour. After complete dissolution of Zinc Chloride, 0.9 M NaOH aqueous solution was added under high speed constant stirring, drop by drop (slowly for 45 min) touching the walls of the vessel. The reaction was allowed to proceed for 2 h after complete addition of sodium hydroxide. The beaker was sealed at this condition for 2 h. After the completion of reaction, the solution was allowed to settle for overnight and further, the supernatant solution was separated carefully. The remaining solution was centrifuged for 10 min and the precipitate was removed. Thus precipitated ZnO NPs were cleaned three times with deionized water and ethanol to remove the byproducts which were bound with the nanoparticles and then dried in air atmosphere at about 60 ºC. During drying, $Zn(OH)_2$ is completely converted in to ZnO. The prepared ZnO nanoparticles were characterized for their optical and nano-structural properties. X-ray diffraction pattern for the ZnO NPs was recorded using an X-ray diffractometer (PANLYTICAL) using Cu K_α radiation of wavelength λ = 0.1541 nm in the scan range 2θ = 20-90º. Morphology of the sample was investigated using scanning electron microscope (SEM with EDXA, Sirion) which also has been used for compositional analysis of the prepared ZnO nanoparticles. The optical transmission/absorption spectra of ZnO dispersed in water were recorded using a UV-VIS spectrophotometer (Hitachi, U-3010). The photoluminescence (PL) spectrum of the ZnO nanoparticles dispersed in water has been measured using a spectrofluorimeter (F-2500 FL Spectrophotometer, Hitachi).

3. Results and Discussions

3.1. X-ray Diffraction (XRD)

Fig. 1 represents the X-ray diffraction pattern of ZnO nano powder.

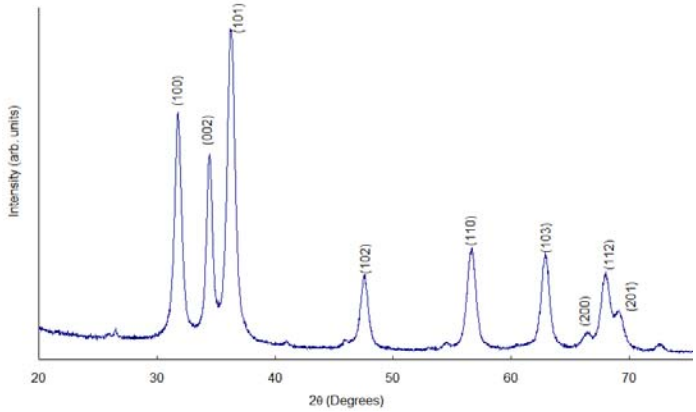


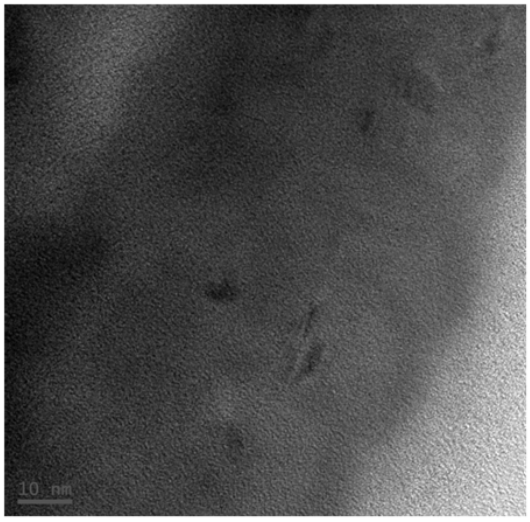
Fig. 1. XRD patterns of ZnO nano particles.

A definite line broadening of the XRD peaks indicates that the prepared material consist of particles in nano scale range. From this XRD patterns analysis, we determined peak intensity, position and width, full-width at half-maximum (FWHM) data. The diffraction peaks located at 31.84º, 34.52º, 36.33º, 47.63º, 56.71º, 62.96º, 68.13º and 69.18º have been keenly indexed as hexagonal wurtzite phase of ZnO [28, 29] with lattice constants a=b= 0.324 nm and c= 0.521 nm (JPCDS card no: 36-1451) [30] and further it also confirms the synthesized nano powder was free of impurities as it does not contain any characteristics XRD peaks other than ZnO peaks. The synthesized ZnO nanoparticle diameter was calculated using Debye-Scherrer formula [31]

$$d = \frac{0.89\lambda}{\beta Cos\ \theta},$$

where 0.89 is the Scherrer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle and β is the full width at half-maximum (FWHM) of the diffraction peak corresponding to plane <101>. The average particle size of the sample was found to be 16.21 nm which is derived from the FWHM of more intense peak corresponding to 101 plane located at 36.33° using Scherrer's formula.

Fig. 2 represents the SEM pictures of ZnO nano particles at different magnifications. These pictures confirm the formation of ZnO nanoparticels. These pictures substantiate the approximate spherical shape to the nanoparticles and most of the particles exhibit some faceting. From the pictures, it also can be seen that the size of the nano particle is less than 10 nm which was in good agreement with the particle sizes (8.32 nm) calculated from the Debye-Scherrer formula.



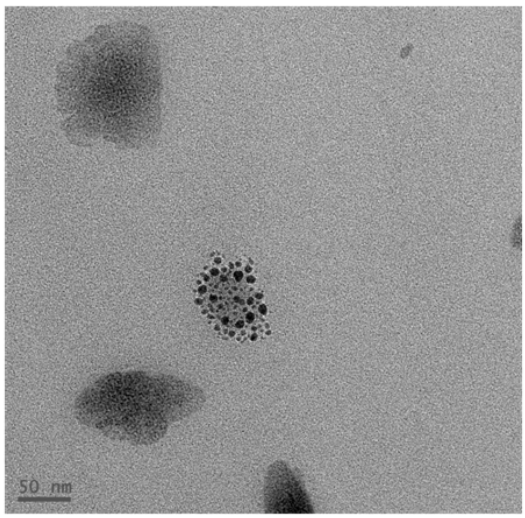


Fig. 2. SEM pictures of ZnO nanopracticles at different magnification.

The Selected Area Electron Diffraction (SAED) pattern (Fig. 3) shows distinct bright rings which confirm the preferential orientation of nanocrystals instead of irregular [29, 32]. Transmission Electron Microscopic pictures (Fig. 4(a, b & c)) have also revealed the ZnO nanoparticles formation produced at different magnifications by confirming the hexagonal plane to the prepared nanoparticles.

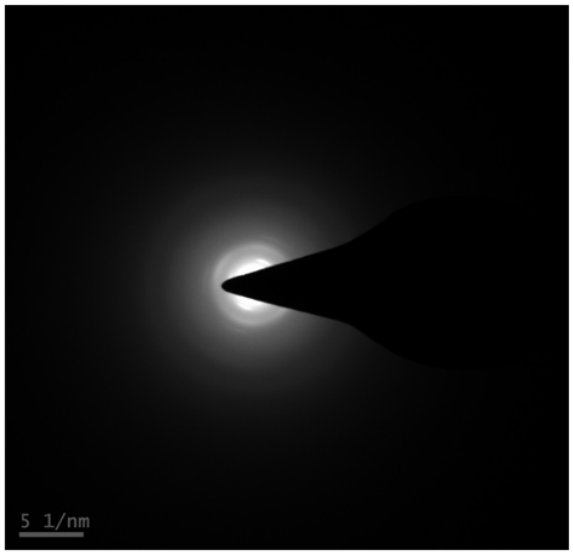


Fig. 3. SAED patterns of prepared ZnO nanopowder.

3.2. UV-vis Absorption Spectrum

The size of the nanoparticles plays an important role in changing the entire properties of materials. Thus, size evolution of semi conducting nanoparticles becomes very essential to explore the properties of the materials and the influence of particle sizes on the spectroscopic properties. UV-visible absorption spectroscopy is widely being used technique to examine the optical properties of nano-sized particles. The absorption spectrum of ZnO nano powder is shown in Fig. 5. It exhibits a strong absorption band at about 355 nm [33]. An excitonic absorption peak is found at about 258 nm due to the ZnO nanoparticles which lies much below the bandgap wavelength of 358 nm (E_g = 3.46 eV). It is also evident that significant sharp absorption of ZnO indicates the monodispersed nature of the nanoparticle distribution [8].

The average particle size in a nanocolloid can be calculated from the absorption onset from UV-vis absorption spectra by using effective mass model [ref to be given – 34 no need to change] where the band gap E^* can be approximated by

$$E^* = E_g^{bulk} + \frac{\hbar^2\pi^2}{2er^2}\left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0}\right) - \frac{1.8e}{4\pi\varepsilon\varepsilon_0 r} - \frac{0.124e^3}{\hbar^2(4\pi\varepsilon\varepsilon_0)^2}\left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0}\right)^{-1}$$

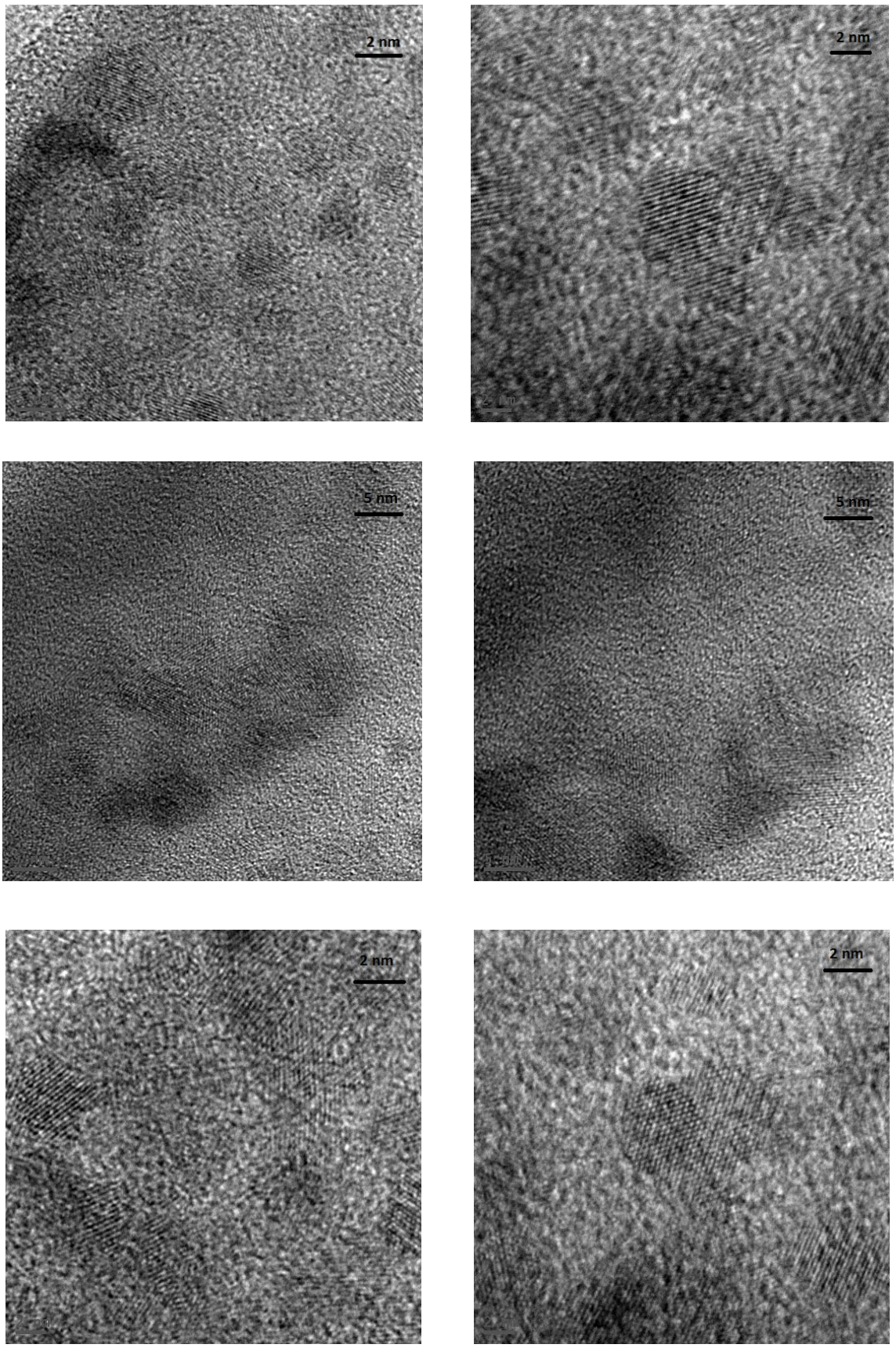


Fig. 4 (a, b, c). High resolution electron microscope pictures of ZnO.

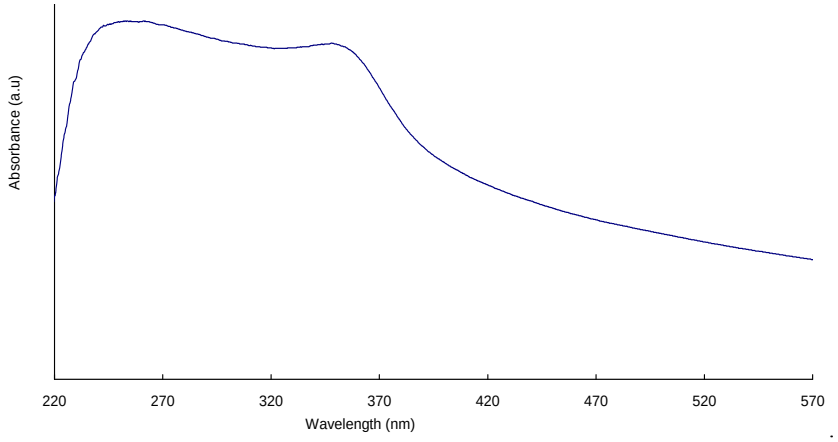


Fig. 5. UV-vis absorption spectra of as prepared ZnO nano.

where E_g^{bulk} is the bulk band gap expressed in eV, $\hbar$ is Plank's constant, r is the particle radius, m_e is the electron effective mass, m_h is the hole effective mass, m_0 is free electron mass, e is the charge on the electron, ε is the relative permittivity, and ε_0 is the permittivity of free space. Due to the relatively small effective masses for ZnO (m_e = 0.26, m_h = 0.59 [21, 22 S. Shionoya, in: S. Shionoya, W.M. Yen (Eds.), Phosphor Handbook, CRC, Boca Raton, FL, 1998. [22] L.I. Berger, Semiconductor Materials, CRC, Boca Raton, FL, 1997.]), band gap enlargement is expected for particle radii less than about 4 nm. The following equation was derived from the effective mass model given above with small mathematical simplification [34] which is used to find the size of the particle from the absorbance spectra,

$$r(nm) = \frac{-0.3049 + \sqrt{-26.23012 + \frac{10240.72}{\lambda_p(nm)}}}{-6.3829 + \frac{2483.2}{\lambda_p(nm)}}$$

where λ_p is the peak absorbance wavelength in nm. The prepared ZnO nanoparticles exhibit an absorbance peak at about 258 nm which corresponds to the particle size of 2.07 nm. This result has also been confirmed by the SEM pictures.

3.3. Photoluminescence Spectrum

It is worth mentioning that the physical properties of semiconducting materials undergo changes when their dimensions get down to nanometer scale known as the "quantum size effects". For example, quantum confinement increases the band gap energy of ZnO, which has been observed from photoluminescence [35]. The photoluminescence originates from the recombination of surface states. The strong PL implies that the surface states remain very shallow, as it is reported that quantum yields of band edge will decrease exponentially with increasing depth of surface state energy levels [36, 37]. Fig. 6 shows the photoluminescence spectrum of ZnO nano powder with excitation wavelength 320 nm at room temperature. The spectrum exhibits two emission peaks, one is located at around 392 nm (uv region) corresponds to the near band gap excitonic emission [38] and the other is located at around 520 nm attributed to the presence of singly ionized oxygen vacancies [39]. The emission is caused by the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy [28, 38]. Further, the spectrum also reveals the narrow size distribution of nano particles in the powder as the luminescence peak full-width half-maximum (FWHM) is only in few nano meters [40].

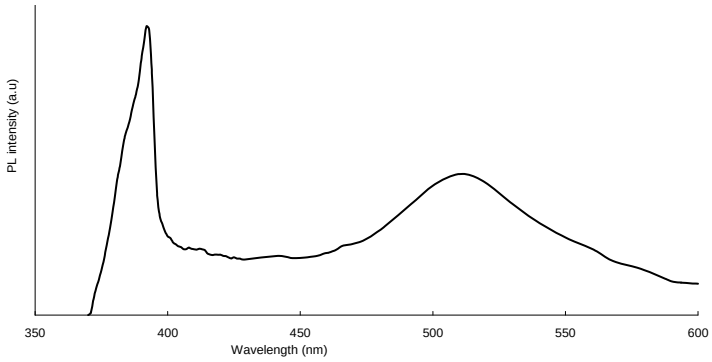


Fig. 6. Photoluminescence spectra of prepared Zn/o nano particles excited with 320 nm.

4. Conclusions

ZnO nanoparticles have been prepared using wet chemical synthesis method and were characterized by XRD, SEM, SAED, UV-vis absorption and photoluminescence spectroscopy. XRD and SEM studies confirmed the nanostructures for the prepared ZnO nanoparticles. SAED pattern consists of bright uniform rings confirming preferential orientation for nanocrystals instead of random orientation. From UV-vis absorption spectrum, the calculated average size of the prepared ZnO nano particles found to be 2.2 nm for peak absorbance wavelength. The prepared ZnO nanoparticles exhibits (λ_{exc} = 320 nm) sharp UV band corresponds to near band gap excitonic emission and broad green emission band due to the oxygen vacancy at room temperature. The prepared ZnO nanoparticles can be used in different industrial applications viz., luminescent material for fluorescent tubes, active medium for lasers, sensors etc.

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